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Sampling Parameters for Sulfate Measurement and Characterization

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■ Evaluations of critical sampling parameters have been performed for primary sulfate measurement and characterization with a selective condensation method. It was found that filtration temperature and sampling flow rate were the critical parameters and that sampling conducted using variations of the parameters would result in incomparable data. It was also found that a viable temperature controlled H_2SO_4 collection device could replace the Goksoyr-Ross coil and alleviate H_2SO_4 recovery and pressure drop problems which are common to the methodology.

Increases in the use of sulfur-containing fuels for energy production have resulted in parallel increases in sulfur oxides emissions from power plants. While environmental concerns over these sulfur oxides formations were to surface much later, the corrosive effects of the oxides have been a persistent problem from the onset. Just as persistent have been the problems related to measuring the sulfur oxides quantitatively, particularly the higher oxides of sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4). Depending on the nature of the fuel, boiler design, and firing conditions, the fuel sulfur is oxidized mainly to sulfur dioxide (SO_2). Subsequent to being oxidized to SO_2 , or by some alternate oxidation reaction route, from 1% to as high as 25% of the sulfur appears in the sulfate form (1). Ordinarily, a large part of the sulfate exists as gaseous H_2SO_4 or absorbed H_2SO_4 on ash particles. It is precisely this phenomenon, the potential of gaseous H_2SO_4 to interact with fuel gas particles, that has not only complicated corrosion difficulties, but has made the measurement of the sulfate species so difficult.

In order to address the problems and parameters involved with acid formation in these combustion systems, extensive work was performed in Western Europe during the middle of this century. This work involved the study of acid formation as a function of excess air (2), sulfur content of the fuel (3), and effects of ash deposits (4). For potential control approaches, the effects of fuel additives were also investigated (5). Regardless of the objectives of the studies, difficulties were common and numerous when attempts were made to sample and quantitate the H_2SO_4 present in the flue gases.

Basically, all of the measurement attempts involve the extractive sampling of the flue gas, followed by the attempted separation of the particulate related sulfate from the unassociated (or gaseous) H_2SO_4 . This separation attempt ordinarily involved either placing some type of porous plug in the inlet end of the sampling probe or passing the flue gas sample through a flat filtering pad following the probe. By assuming that all of the gas-phase H_2SO_4 had passed the filter, the acid was then collected by an impinger train or by collecting the

acid in aerosol form following its condensation. For most corrosion studies the filter was discarded, since the primary objective was measuring the H_2SO_4 (to which the corrosion was attributed). The success of these studies was contingent upon both the collection efficiency of the impingers or aerosol collector, as well as the success of passing the H_2SO_4 gas through the filtering device.

With the shift of energy production in the U.S. from coal to the less expensive crude oil during the last decade, a resurgence of interest in sulfur oxides measurements has occurred. Notwithstanding the corrosion problems which have remained persistent, the more recent emphasis has been directed toward environmental aspects. These interests were spurred by both the correlation of total suspended particulate in the Northeast with increased crude oil usages (6) and by the considerably higher than predicted ratio of H_2SO_4 to SO_2 for oil-fired units (7). A recent study (8) of sulfate presence in the total suspended particulate (TSP) in the atmosphere near an oil-fired plant has suggested a significant local impact caused by emissions of primary sulfates. Contemporary studies involving primary sulfates include both H_2SO_4 corrosion and emission control strategy, particularly flue gas desulfurization type control systems.

Accompanying the resurgence of sulfate emissions concerns was renewed interest in measurement methodology. The emphasis of these measurements has been placed on both a total sulfate sampling approach (9) and a characterization approach (10, 11), which would distinguish between unassociated gaseous H_2SO_4 and particulate related sulfate. The particulate related sulfate consists of both metal sulfate and absorbed H_2SO_4 . In the Gaseous Emissions Research Section of EPA's Environmental Sciences Research Laboratory, we have addressed the problems of sulfate measurement technology. Our initial work (9) involved total water-soluble sulfates (TWSS) measurements for fossil fuel fired boilers and culminated in a recommended procedure for such sampling. Refinement of primary sulfate emissions measurements from these sources ultimately led to examining methodology for measuring gaseous H_2SO_4 separately from particulate related sulfates. Upon examination of previous work it was found that the approach used for this type of measurement ordinarily involved the selective condensation method. Former users of the method have apparently overemphasized the collection efficiency of the condensation coil, while neglecting attention to the filtration process. While considerable effort (12, 13) has been expended on the reaction of sulfur trioxide (SO_3) with fly ash to increase the efficiency of electrostatic precipitators, the potential for the same reaction during sampling has apparently been ignored. Work (14) has also shown that when the SO_3 (which exists as gaseous H_2SO_4 in combustion gases)

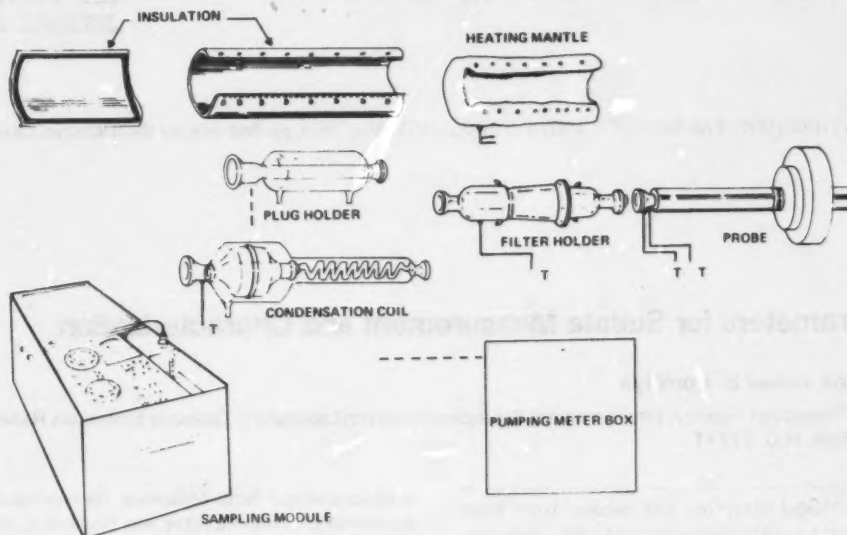


Figure 1. Schematic drawing of manual acid condensation system

reacts with fly ash particles, the reaction is only partially reversible, as indicated by the observed hysteresis. When attempts are made to distinguish unassociated gaseous H_2SO_4 from particulate related sulfates, the methodology must account for this potential interference due to H_2SO_4 absorption at the particulate filtration interface.

Further problems with the selective condensation approach were encountered during our own field sampling experiences including acid recovery from the backup frit of the Goksoyr-Ross (15) coil and the high pressure drop introduced into the sampling system by the frit. The high pressure drop from the frit along with the continuously changing pressure drop at the filter during particle collection resulted in difficulties in maintaining a consistent and repeatable sampling rate.

This work involves the development and evolution of a selective condensation system which would serve as a primary sulfate characterization method for combustion source measurements. A thorough study of the sampling parameters of flow rate and filter temperatures and their effects on separating gaseous H_2SO_4 from particulate-related sulfate was performed. Also investigated were the frit retention of sulfate ion during sample recovery and a viable equivalent acid aerosol collection method. Predictions from the results indicate that comparisons of such sulfate characterization measurements, which attempt to distinguish gaseous H_2SO_4 from particulate sulfate, cannot be acceptable unless sampling guidelines are adhered to.

Experimental

A sulfate measurement and characterization system which uses a Goksoyr-Ross type condensation coil was designed for field sampling as shown in Figure 1. The system consists of a high-temperature heated quartz probe, which includes a sheathing which slides snugly into a custom made "Swagelok" fitting adapted to a standard 4-in. port cap. Following this is a high-temperature quartz filtering device, enclosed within a custom made heating mantle, and which has a coarse quartz support frit for holding the filtering pad. Following the filtration, the H_2SO_4 is converted to the aerosol form in the temperature-controlled collection device, which for this work consisted either of a Goksoyr-Ross condenser or glass wool plug holder. For some experiments, the plug holder preceded the condenser. In order to prevent moisture condensation in the condenser or plug holder, which would enhance the potential for SO_2 oxidation, the temperature is maintained near

60 °C by circulatory water from a hot water bath. Following the H_2SO_4 collection device is an 80% 2-propanol (IPA)- H_2O Greenburg-Smith bubbler, followed by a 3% peroxide (H_2O_2) impinger for SO_2 collection. Accompanying the ice bath containing the impingers, the sampling module also contains the water bath, along with voltage controls for heating the probe and filter. The module also contains a four-position pyrometer for reading the temperature potentials from four strategically located copper-constantan thermocouples, as indicated by "T" in Figure 1. The sample is acquired by a standard Research Appliance Corporation (RAC) sampling unit, such as used for method 5 particulate sampling. The weight of the sampling module, less water in the bath, is 30 lb (13.6 kg), and it can be easily transported by an individual sampler.

At the initiation of each sample, all temperatures and the time are recorded. At the termination of sampling, the same parameters are recorded. For the results presented here, all temperatures are presented as averages of the initial and final ones recorded. In actuality, one must observe these temperatures nearly continuously and, when fluctuations occur, make appropriate control adjustments in order to maintain the desired level. The continuous observation of flow rate is even more necessary as the pressure drop across the filtration device increases as the particulate buildup occurs. Stopwatch timing of the gas meter volume is necessary if a consistent flow rate is to be maintained. The samples are recovered in their respective fractions of the probe wash, filter, and filter wash, condenser and/or plug wash, IPA, and H_2O_2 catch. Additional sample fractionation was performed when the objectives of the measurement dictated. The high-temperature filters used during this work consisted of high-purity quartz as described by ADL (16) and were heat treated to 900 °F for 4 h prior to use.

The recovered samples are titrated by the barium-thorin procedure as described in the EPA Compliance Test Method 6 (17), except that the probe wash and filter wash are passed through the mixed bed resin to remove metal interfering cations prior to titration.

A series of tests was performed at a local No. 6 residual-oil-fired boiler to establish the effects of flow rate and temperature. During the studies when the flow rate was varied, the filter temperature was maintained at 271 to 282 °C. For samples involving various filter temperatures, sampling was conducted at 10 L/min. During the sampling, the flue gas

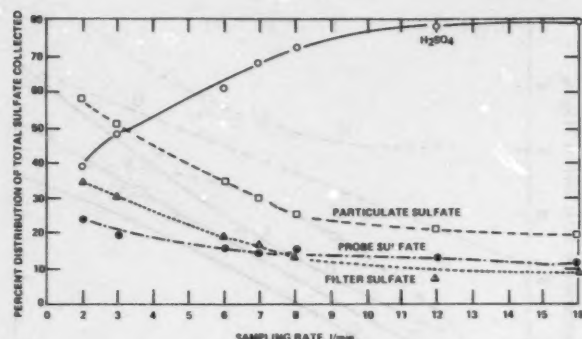


Figure 2. Effects of sampling rate on sulfate distribution

temperature fluctuated between 260 and 288 °C. A series of samples was also performed to examine the extent of sulfate retention in the backup frit contained in the condenser. This was a result of some prior work (unpublished), which indicated that as high as 30% of the H₂SO₄ was being collected on the frit of the condenser regardless of the number or configuration of coils which preceded the frit.

As an equivalent method of H₂SO₄ aerosol collection, a special water jacketed glass wool plug holder was used for a series of samples. During a portion of the samples the plug holder was used as an H₂SO₄ backup collector to the condenser, while some samples were collected solely with the glass plug after filtration. Throughout this work, the temperature of either or both the acid collection devices was maintained at 60 °C. Subsequent sampling at a coal-fired boiler was conducted to establish the feasibility of using the same glass plug for several successive samples without sulfate retention.

Results and Discussion

A series of 16 samples, consisting of duplicate runs of 8 different flow rates, was collected at the oil-fired boiler. For the purpose of establishing flow rate effects it was assumed that all sulfate which passed the probe and high temperature filtration device was H₂SO₄. On this basis the percent H₂SO₄ was calculated as the ratio of sulfate collected past the filter divided by the total sulfate collected in the sampling train × 100%. The results of the various sampling rates are shown in Figure 2. The fraction of H₂SO₄ penetrating the filter is a function of the velocity of the gas stream between 2 and 8 L/min, approaching a plateau between 12 and 16 L/min. For the 8 to 16 L/min flow rate there appears to be little effect of flow rate either on the probe or filter distribution. At the lower flow rate of 2 to 6 L/min, the steeper slope of filter catch indicates the H₂SO₄ is being collected in the front half of the train predominantly at the filter, with a lesser retention by the probe. More than likely some of the particles collected at the filter at higher flow rates dropped out in the probe at lower flow rates, and the ratio of acid on the filter to particulate sulfate was greater than indicated in the figure.

Having confirmed the potential error due to sampling at low flow rates, a second series of samples was collected to establish the effects of filter temperature on sulfate distribution. The results of the series of duplicate runs at each of 5 temperatures using a 10 L/min flow rate are shown in Figure 3. Again the results of the measurements, particularly with respect to sulfate characterization, are dependent on a sampling parameter. There appears to be no effect of sulfate in the probe; this would be expected inasmuch as the probe temperature was maintained above 271 °C. As the filter and filter holder temperature were varied, the effects are seen in these components of the sampling train. While there is a gradual increase in sulfate retention from 260 down to 150 °C, this be-

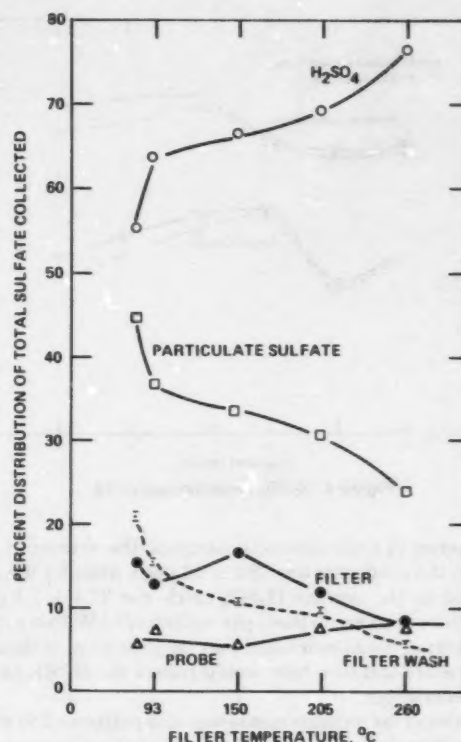


Figure 3. Effects of filter temperature on sulfate distribution

comes more profound from 150 down to 82 °C. It is apparent that the condensation of sulfuric acid is occurring and, furthermore, some of the acid is condensing on the filter holder before reaching the filter. The overall effects of filter temperature on the ability of the methodology to distinguish gaseous H₂SO₄ from particulate related sulfate were apparent throughout the temperature range involved. According to the results, maintaining the filter temperature at 260 °C rather than 150 °C reduced, in effect, the particulate ratio of total sulfate from 33.5 to 23.5%. Likewise, assuming the ratio of H₂SO₄ to total sulfate to be 76.4% as it was at 260 °C, it can be calculated that 13% of the H₂SO₄ was retained at the filter at 150 °C and would be included as particulate matter.

A further series of studies was performed to establish an equivalent method of collecting condensed H₂SO₄. During field measurements a constant flow rate was difficult to maintain with the condensation sampling train due to pressure drops within the system. As the backup frit in the condenser was found to introduce a 7 to 9 in. Hg pressure drop in the sampling system, along with the additional pressure drop due to the filter and collected particulate, a method which would avoid such pressure drops was desirable. In addition, prior experience had proven that a slow buildup of sulfate in the backup frit was occurring over a period of several samples, a buildup which could not be recovered by the routine washing, but required a hot water washing for several hours. The method of collecting H₂SO₄ after the filter should preferably offer both a low-pressure drop and minimal effort for complete sample recovery. From our prior experience with collecting H₂SO₄ with glass wool plugs, enclosing such a plug in a water-jacketed holder appeared to be a feasible approach. The construction of the holder (depicted in Figure 1) was such that the same circulating water bath was used as for the condenser.

Several series of simultaneous samples with the condenser and glass plug holder were performed to determine if the glass plug would collect the H₂SO₄ as efficiently as the condenser.

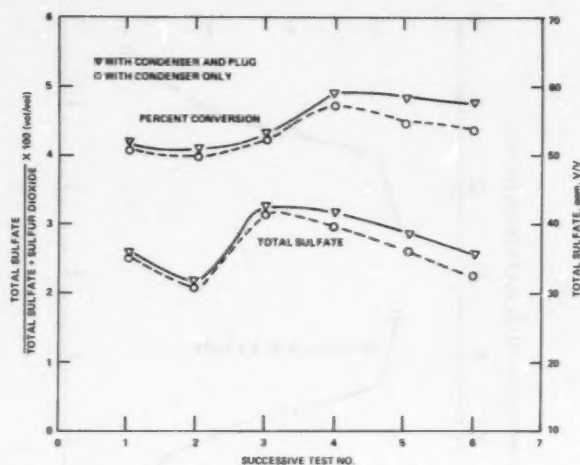


Figure 4. H_2SO_4 breakthrough of frit

For a series of 6 simultaneous samples, the average H_2SO_4 catch in the condenser was 38.2 ± 3.1 ppm, while for the glass plug holder the average H_2SO_4 catch was 37.4 ± 7.4 ppm. (Concentrations are in parts per million v/v.) Within experimental error, it was concluded that the glass plug, at the same temperature and flow rate, would collect the H_2SO_4 as well as the condenser.

A series of six measurements was also performed to ascertain whether the buildup of sulfate in the frit would eventually result in acid breakthrough. A thoroughly cleaned condenser was used for the six measurements, which also involved the glass plug holder just subsequent to the condenser in the sampling train. As the testing proceeded chronologically from test 1 through 6, it can be seen in Figure 4 that a gradual breakthrough of H_2SO_4 is occurring at the condenser frit and is being collected in the glass plug. In the upper portion of Figure 4 the effect can be seen that this breakthrough will have on calculating the percent conversion of SO_2 to SO_4 , based on total sulfate/(total sulfate + sulfur dioxide) $\times 100\%$.

A final series of sulfate characterization measurements was performed on a coal-fired boiler, using the acid condensation system at various sampling rates. Of interest during this work was the establishment of a relationship between percent H_2SO_4 and the sampling rate at this combustion source, and the subsequent comparison of the relationship with that obtained from the oil-fired boiler. The results of the coal-fired boiler along with the oil-fired boiler results are presented together in Figure 5, along with the 95% confidence intervals. The flue gas temperature during these measurements fluctuated between 150 and 158 $^{\circ}C$. It was thought that if the relationship between the percent of H_2SO_4 and sampling rate was the same, corrections could be applied for data obtained at various sampling rates for different sources. This approach appears to be inapplicable, as the slopes of the lines (3.856 for the coal-fired and 5.684 for the oil-fired) vary considerably. It must be concluded that data comparison from one source to another will be meaningful (in terms of sulfate characterization) only if the samples are collected at the same sampling rates.

Conclusions

It has been found from these studies that the selective condensation approach to measuring and characterizing primary sulfate emissions from combustion sources must be used with precaution. In general, when attempts are made to distinguish gaseous H_2SO_4 from absorbed H_2SO_4 and other inorganic sulfates, their success is contingent upon several sampling parameters.

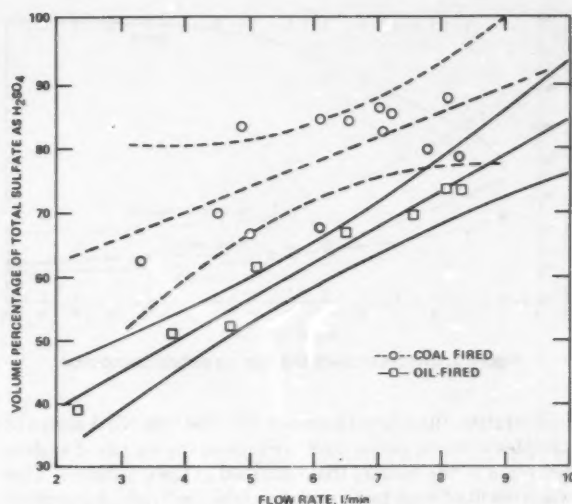


Figure 5. Comparison of coal and oil-fired boilers

Of particular concern is the rate at which the sampling is conducted. While the sample rate results presented in this work consisted of time averages of sample volume per total sampling time, the actual sampling rate was ascertained with a stopwatch throughout the run. Due to the increasing pressure drop in the sampling system from the particulate buildup at the filter, a consistent sampling rate can be maintained only by constant timing of the gas meter. Due to the degree of the slope of the line shown in Figure 2, between 2 and 8 L/min, it is not adequate to "average" 10 L/min, as a lower sampling rate during the latter portion of sampling with still bias the results toward particulate sulfate.

The temperature study indicates that a maximum of 271 to 281 $^{\circ}C$ is necessary to assure a minimum H_2SO_4 retention at the filter. It would have been of interest to have performed sampling with the filter temperature above this recommended temperature; however, conversion of H_2SO_4 to unassociated SO_3 and ultimately back to SO_2 presents a high temperature constraint on the method. Extending the filter temperature beyond the flue gas temperature in itself presents the potential problem of desorbing H_2SO_4 from some of the particles. Whether this occurs could only be ascertained by the simultaneous in situ measurement of gaseous H_2SO_4 , a measurement that currently is not technologically feasible.

It was also found from the study that two serious measurement problems, namely system pressure drop and acid-frit recovery, can be eliminated by a viable H_2SO_4 collection alternative. The temperature-controlled glass plug proved to collect the H_2SO_4 aerosol as well as the condenser, and avoided the pressure drop and acid recovery problems. Furthermore, the glass plug approach is simple, less costly to construct, and does not result in H_2SO_4 buildup and/or breakthrough as does the condenser.

In view of the above results, it is recommended that primary sulfate measurements conducted by the selective condensation approach be done so in excess of 10 L/min and with a filter temperature of 271 to 281 $^{\circ}C$. It is further recommended that the awkward Goksoyr-Ross type condenser be replaced in the sampling train with a simple, well-packed 1 cm $\times$ 15 cm Pyrex glass plug, in a temperature-controlled holder device. Recovery of H_2SO_4 from this device requires only a simple rinse with the help of a small vacuum; as a precaution, the glass wool must be dried with air prior to its further use.

Finally, in view of several extensive efforts to characterize primary sulfate emissions from combustion sources with this type of measurement approach, it is recommended that the sampling parameters examined in this work along with the

recommendations be adhered to, such that data from various sources can be compared at a later point in time. On the basis of sulfate characterization, this can be done only if a consistent sampling rate and filtration temperature for the method are used during the source sampling.

Literature Cited

- (1) Homolya, J. B., Barnes, H. M., Fortune, C. R., in Proceedings of the Fourth National Conference on Energy and the Environment, Cincinnati, Ohio, Oct 1976, pp 490-4.
- (2) Chaikivsky, M., Siegmund, C. W., *J. Eng. Power*, **96**, 64-WA/CD-2, 379-88 (1965).
- (3) Corbett, P. F., *J. Inst. Fuel*, **24**, 247 (1951).
- (4) Black, A. W., Stark, C. F., Underwood, W. H., *Am. Soc. Mech. Eng., [Pap.]*, No. 60-WA-285 (1960).
- (5) Alexander, P. A., Fielder, R. S., Jackson, P. J., Raask, E., Williams, T. B., *J. Inst. Fuel*, **34**, 53 (1961).
- (6) Kleinman, M. T., Bernstein, D. C., Kneip, T. J., *J. Air Pollut. Control Assoc.*, **17**, 1 (1977).
- (7) Homolya, J. B., Cheney, J. L., in Proceedings of Workshop on Measurement Technology and Characterization of Primary Sulfate Emissions, from Combustion Sources, EPA-600/9-78-020b, P-3, Research Triangle Park, N.C., 1978.
- (8) Homolya, J. B., Cheney, J. L., 175th National Meeting of the American Chemical Society, Anaheim, Calif., 1978, Abstract ENVT-054.
- (9) Cheney, J. L., Winberry, W. T., Homolya, J. B., *J. Environ. Sci. Health*, **A12**(10), 549 (1977).
- (10) Dietz, R. N., Weiser, R. F., Newman, L., in Proceedings of Workshop on Measurement Technology and Characterization of Primary Sulfate Emissions from Combustion Sources, EPA-600/9-78-020a, P-3, Research Triangle Park, N.C., 1978.
- (11) Maddalone, R. F., in Proceedings of Workshop on Measurement Technology and Characterization of Primary Sulfate Emissions from Combustion Sources, EPA-600/9-78-020b, P-219, Research Triangle Park, N.C., 1978.
- (12) Bickelhaupt, R. E., *Environ. Sci. Technol.*, **9**(4), 336 (1975).
- (13) White, H. J., *Electr. World*, **22** (1970).
- (14) Ditl, P., Coughlin, W., *Environ. Sci. Technol.*, **11**, 701 (1977).
- (15) Goksoyr, H., Ross, K., *J. Inst. Fuel*, **35**, 225 (1962).
- (16) Benson, A. L., Levins, P. L., Massucco, A. A., Valentine, J. R., "Development of a High Purity Filter for High Temperature Particulate Sampling and Analysis", EPA-605/2-73-032, Nov 1973.
- (17) *Fed. Regist.*, **42**(160), 41754-89 (Aug 18, 1977).

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